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A MICROSTRUCTURE, PIEZOELECTRIC AND DIELECTRIC PROPERTIES OF THE PZT CERAMICS OBTAINED BY THE SOL-GEL METHOD

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A technological process to obtain ceramic materials by the sol-gel method replaces gradually conventional methods, based on a simple oxide synthesis as a result of high temperature sintering. The materials obtained by the sol-gel method are characterized by high density and better chemical purity. A powder with the $Pb(Zr_{0.52}Ti_{0.48})O_3$ chemical composition was obtained as a result of a synthesis by the sol-gel method and it was formed and sintered by a hot pressing method (HP). The specimens obtained were subjected to examinations of the dielectric properties, the tangent of dielectric loss angle, the piezoelectric properties and their micro-photographs were taken (SEM).

A course of the technological process by the sol-gel method was described, the dielectric and piezoelectric parameters were determined and a microstructure and a domain structure were examined in the work.

Keywords: dielectric, piezoelectric properties

1. Introduction

The PZT ceramic material is a solid solution with the $Pb(Zr_xTi_{1-x})O_3$ general molecular formula, showing a crystalline structure of the perovskite type. Electro-mechanical and dielectric parameters of the $Pb(Zr_xTi_{1-x})O_3$ solid solution can be controlled by a change in a ratio of $PbZrO_3$ to $PbTiO_3$. A diagram of a PZT phase solid solution is presented in Fig. 1a. From the PZT phase solid solution diagram it results that in a case of a replacement of the Ti^{4+} ions with the Zr^{4+} ions in $PbTiO_3$ there is a decrease in the tetragonal deformation and it contributes finally to occurrence of a rhombohedral structure $F_{R(HT)}$ with a R3m symmetry, Fig. 1b.

At 623 K temperature for Zr:Ti 55/45 so-called morphotropy boundary MPB, being co-existence of the rhombohedral and tetragonal phase, occurs in the ferroelectric phase.

If the Zr^{4+} concentration is higher than 95% mol, then in the PZT solution there is an anti-ferroelectric rhombus phase A_0 typical for $PbZrO_3$ with a narrow area of a stable anti-ferroelectric tetragonal phase (A_T) near a Curie point. Cooling PZT solution with a composition near the MPB morphotropy boundary causes a transition from the para-electric phase with the Pm3m regular structure at the Tc phase change temperature into the $F_{R(HT)}$ ferroelectric phase with the R3m structure and the F_T ferroelectric tetragonal phase with the P4mm structure.

a) b)

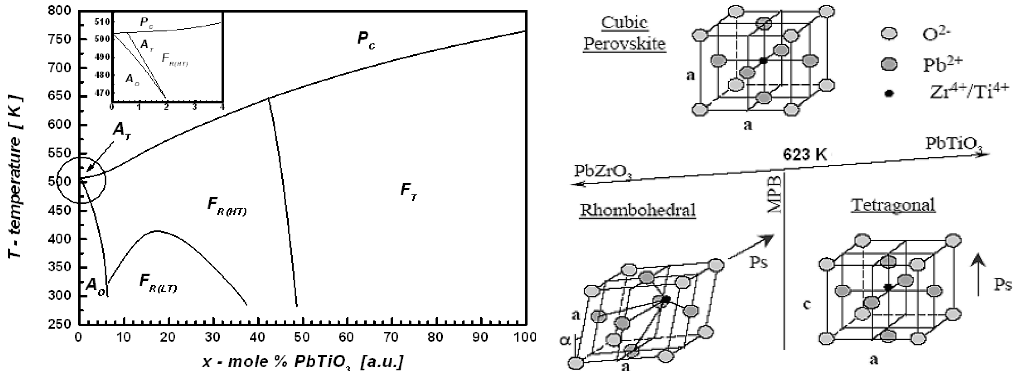

Fig. 1. a) The phase diagram [1], b) The shape of elementary cells in the PZT ceramics.

An aim of the work was to obtain the PZT solid solution by the sol-gel method with the $Pb(Zr_{0.52}Ti_{0.48})$ composition from the MPB morphotropy area (Fig. 1a). The sol-gel method is based on a transition of a system from the liquid sol into a phase of solid gel, what enables to obtain ceramic materials in various forms, among others solid ceramics. The raw materials used cause that the ceramics obtained shows high density and chemical purity what has a significant influence on its properties.

In the work the dielectric and piezoelectric properties of the specimens compacted by the hot pressing method (H_T) were examined, photographs (SEM) of the microstructure and the domain structure were taken. The piezoelectric properties of the PZT 52/48 material obtained were compared with the PZT ceramics with the PZT 35/65 composition characterized by the tetragonal structure and with PZT 65/35 characterized by the rhombhedral structure [1, 6].

2. Experiment

The PZT 52/48 ceramic specimens with the $Pb(Zr_{0.52}Ti_{0.48})O_3$ molecular formula were obtained by the sol-gel technology by a synthesis reaction in the liquid phase of organic metal salts. The PZT type ceramics in question on the phase diagram (Fig. 1a) is in the MBP morphotropy area for which coexistence of the rhombohedral and tetragonal phase is characteristic.

The PZT ceramic material was obtained by use of the following precursors: lead acetate, zirconium propanol, titanium propanol and acetylacetone. The PZT material synthesis lasted 45 minutes. After the synthesis process the product obtained was subjected to distillation, during which a by product ester – propyl acetate was removed. After the distillation acetylacetone and distilled water were added. Sol was formed and then gel as a result of hydrolysis reactions. After drying the liquid phase, xerogel was obtained and it was subjected to sintering at the temperature of 873 K for 2 hours, in order to remove organic compounds. The PZT ceramic material obtained was ground for 2 hours. Then, pellets with 10 mm diameter were formed, and subsequently they were hot pressed at the temperature of 1400 K and under 20 MPa pressure for 2 hours. Silver paste electrodes by a sintering method for 5 h at 1073 K temperature were spread on the 1 mm thick specimens obtained.

The specimens obtained were subjected to examinations of the dielectric and piezoelectric properties, the microphotographs of the microstructure and the domain structure were taken. Electric permittivity and the tangent of the dielectric loss angle were tested by a bridge of a BM 595 type. The examinations were conducted in a sinusoidal variable field with the frequency from 100 Hz to 20 kHz in the temperature range from 295 K to 750 K. In order to examine the piezoelectric properties the PZT ceramics was subjected to an influence of a stable electric field, namely polarization of the ceramic material was made. The following polarization conditions were accepted: field polarization intensity 20 kV/cm, a polarization temperature 400 K, polarization process time 2 h. The piezoelectric properties were determined by a resonance and antiresonance method [2–5, 7].

3. Examination results

The microphotographs presented in Fig. 2 illustrating the microstructure (Fig. 2a) and the domain structure (Fig. 2b) of the non-polarized PZT ceramics compacted by the

a) b)

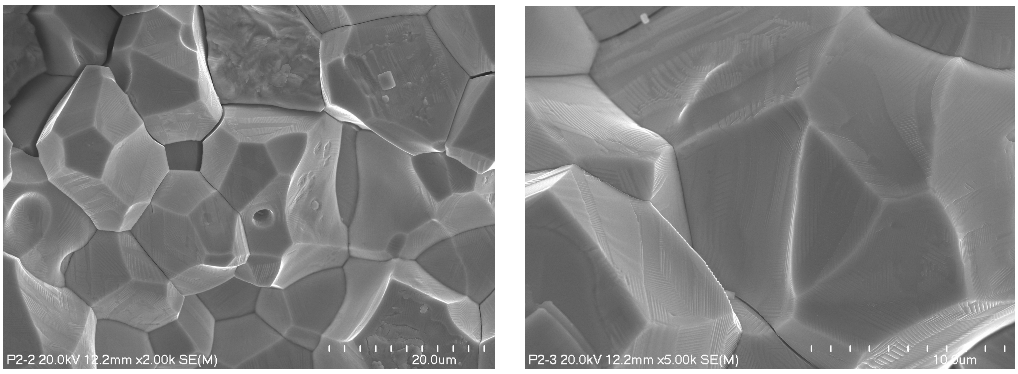

Fig. 2. The micro-photographs (SEM) of the PZT 52/48 ceramics: a) the PZT 52/48 micro-structure, b) the domain structure.

hot pressing method were taken for the PZT 52/48 ceramic composition in question. The PZT ceramics is a polycrystalline sinter characterized by high coherence and strength; it constitutes a multiphase system, in which three phases can be differentiated: crystalline, amorphous and gaseous. A ceramic material microstructure depends on a lot of factors: a technological process, a type of raw materials, kinetics of phase changes, sintering time, a grain growth condition. Well-formed grains and boundaries between grains being 120°, can be observed in Fig. 2a. The non-polarized PZT 52/48 ceramics is characterized by the domain structure – twin one (Fig. 2b). Average density of the PZT 52/48 ceramic specimens obtained compacted by the hot pressing method (HP) is to 6857 kg/m^3 [6].

The piezoelectric parameters for the PZT ceramic in question were determined by the resonance and anti-resonance method reading values of frequency of resonance, anti-resonance and the first over-tone. On basis of the values obtained the piezoelectric parameters of the polarized PZT ceramics compacted by the hot pressing method (HP) were calculated. Values of the PZT 52/48 ceramic parameters are presented in Table 1, and the parameters obtained were also compared with the PZT ceramics with the 35/65 composition and PZT 65/35 [8]. The results obtained show that the PZT ceramics from the tetragonal area has very similar piezoelectric parameters to the PZT ceramics from the rhombohedral area. For example, the k_p electro-mechanical coupling coefficient for the PZT 65/35 ceramics is 0.42 and it is 0.01 higher than for the PZT ceramics with the 35/65 composition. However, the PZT 52/48 ceramics is characterized by the k_p coefficient being 0.51.

Table 1. Values of piezoelectric parameters determined for the PZT ceramics.

Parametr	PZT 65/35 [8]	PZT 52/48	PZT 35/65 [2]
Poisson's ratio	0.38	0.40	0.38
Electro-mechanical coupling coefficient k_p	0.42	0.51	0.41
Transverse electro-mechanical coupling coefficient k_{31}	0.23	0.26	0.22
Piezoelectric modulus d_{31} [C/N]	$48.2 \cdot 10^{-12}$	$61.3 \cdot 10^{-12}$	$36.6 \cdot 10^{-12}$
Sound speed V_R [m/s]	2278	2957	2755
Elastic susceptibility S_{11}^E [m^2/N]	$1.11 \cdot 10^{-11}$	$1.15 \cdot 10^{-11}$	$1.08 \cdot 10^{-11}$
Elastic susceptibility S_{12}^E [N/m^2]	$-4.23 \cdot 10^{-12}$	$-4.19 \cdot 10^{-12}$	$-4.21 \cdot 10^{-12}$
Modulus g_{11} [Vm/N]	$12.35 \cdot 10^{-3}$	$16.45 \cdot 10^{-3}$	$15.18 \cdot 10^{-3}$

The relative error of the parameters obtained did not exceed the value of 1%.

Examples of temperature dependences of the $\varepsilon(T)$ electric permittivity and the $\tan\delta(T)$ tangent of the dielectric loss angle for the PZT ceramics compacted by the hot pressing method (HT) are presented in Fig. 3 respectively. The $\varepsilon(T)$ curves show characteristic maxima in the phase change area. The ε value increases initially with the increasing temperature reaching the ε_m maximum value at the temperature of the phase change T_c. Further temperature increase results in a decrease in the ε value above the Curie temperature, according to the Curie–Weiss law.

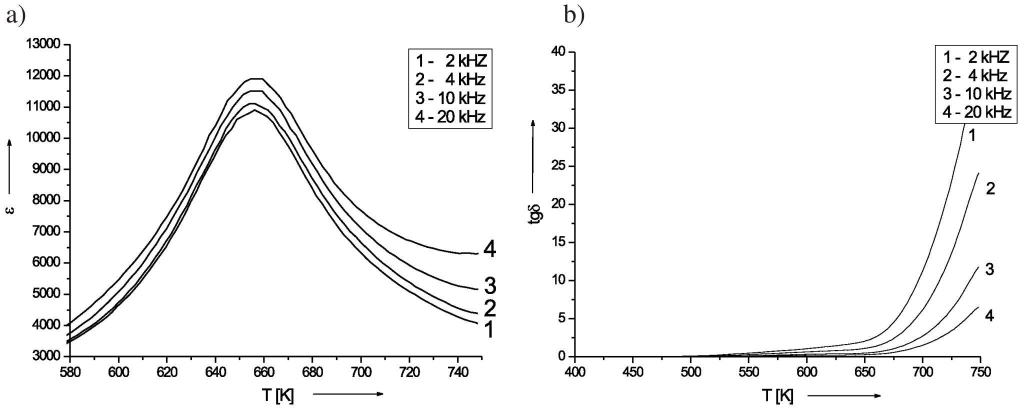

Fig. 3. Temperature dependences obtained for the PZT 52/48 ceramic compacted by a hot pressing method: a) permittivity $\varepsilon(T)$, b) the tangent of the dielectric loss angle – $\tan\delta(T)$.

The ε_m electric permittivity values (Fig. 3a) for the PZT 52/48 composition at the T_m temperature of the paraelectric-ferroelectric phase change is 11990. The $\tan\delta$ value at the T_c temperature for the PZT 52/48 specimens in question for a measurement field with 2 kHz frequency did not exceed unity. In the temperature range of 294–655 K the value of the tangent of the dielectric loss angle is approximately 0.15, whereas a decrease in the values of the dielectric loss angle with frequency increase is observed. A diagram of the dependences of the tangent of the dielectric loss angle on the temperature is presented in Fig. 3b.

4. Conclusions

Since there is a constant increase in requirements which have to be met in practice by the ceramic materials, intensive tests are being conducted in this scope and those tests enable to determine parameters allowing them being applied in many fields of technology and branches of industry, including medicine. New materials and technologies of their production, which make modernization, time and temperature stability of their properties possible, are still being looked for. The PZT ceramics characterized by good dielectric piezoelectric and optical parameters essential for applications mainly in electronic engineering, micro-electronic engineering, radio engineering, communication and medicine, deserves special attention.

References

[1] CZEKAJ D., *Technology, properties and applications of PZT thin films*, Wydawnictwo Uniwersytetu Śląskiego, Katowice 2002.

[2] DUKAT M., ZARYCKA A., *Dielectric and piezoelectric properties of PZT type ceramicsobtained by the sol-gel metod*, Archives of Acoustics, **32**, 4 (Supplement), 65–70 (2007).

[3] OCZOŚ K. E., *Kształtowanie ceramicznych materiałów technicznych*, Oficyna Wydawnicza Politechniki Rzeszowskiej, Rzeszów 1996.

[4] OSIŃSKA K., *Struktura i właściwości fizyczne ceramiki i cienkich warstw ferroelektrycznych PZT, otrzymanych metodą zolowo–żelową*, [in:] Prace Wydziału Techniki, **30**, Ferroelektryki tlenowo-oktaedryczne, Wydawnicwo Uniwersytetu Śląskiego, Katowice 1997.

[5] PŁOŃSKA M., CZEKAJ D., SUROWIAK Z., *Zastosowanie metody zolowo-żelowej w technologii ceramicznych nanoproszków ferroelektrycznych 8/65/35 PLZT*, Ceramika, Polski Biuletyn Ceramiczny, **66**, 594 (2001).

[6] SUROWIAK Z., *Wpływ warunków technologicznych na strukturę i właściwości fizyczne warstw ferroelektrycznych*, Wydawca Uniwersytet Śląski, Katowice 1990.

[7] ZARYCKA A., BRUŚ B., ILCZUK J., CZERWIEC M., DUKAT M., *The internal friction background in PZT ceramics obtained by the sol-gel method*, Material Science, Poland, **25**, 869 (2007).

[8] ZARYCKA A., BRUŚ B., PŁOŃSKA M., ILCZUK J., *Analiza właściwości piezoceramiki PZT otrzymanej metodą zol-żel*, 50. Open Seminar on Acoustics, p. 323, Oddział Górnośląski PTA, Gliwice 2003.